

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
29 January 2004 (29.01.2004)

PCT

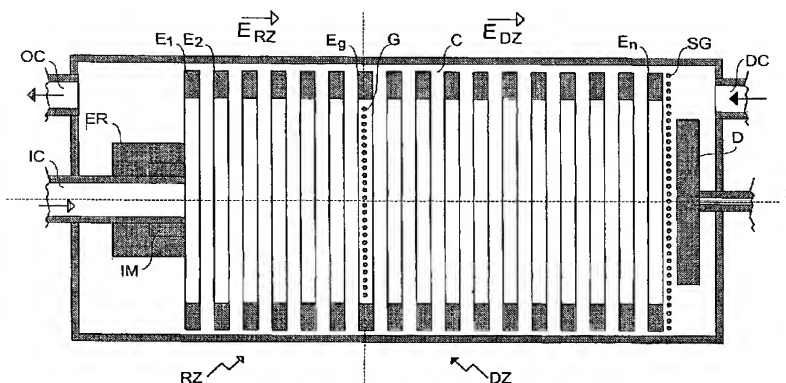
(10) International Publication Number
WO 2004/010131 A1

- (51) International Patent Classification⁷: **G01N 27/64**, 33/00
- (74) Agents: **PIZZOLI**, Antonio et al.; Società Italiana Brevetti S.p.A., Via Carducci, 8, I-20123 Milano (IT).
- (21) International Application Number:
PCT/IT2003/000429
- (22) International Filing Date: 10 July 2003 (10.07.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
MI2002A 001616 22 July 2002 (22.07.2002) IT
MI2002A 001686 29 July 2002 (29.07.2002) IT
- (71) Applicant (for all designated States except US): **SAES GETTERS S.p.A.** [IT/IT]; Viale Italia, 77, I-20020 Lainate (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **PUSTERLA**, Luca [IT/IT]; Via Archimede, 42, I-20129 Milano (IT). **BONUCCI**, Antonio [IT/IT]; Via Chiarelli 8/M, I-20151 Milano (IT). **GIANNANTONIO**, Roberto [IT/IT]; Via Montagnina 9, I-28047 Oleggio (IT). **SUCCI**, Marco [IT/IT]; Via Lo Monaco 9, I-20131 Milano (IT).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR CARRYING OUT ION MOBILITY SPECTROMETRY ANALYSES



(57) Abstract: Methods for carrying out analyses of a gas comprising one or more species S_1, S_2, \dots, S_n by means of ion mobility spectrometry consisting in carrying out two subsequent analyses in different conditions and comparing the results of these two analyses; the different conditions in the two analyses are such as to modify either the residence time of the ions corresponding to said species in the reaction zone or in the drift zone of the ion mobility spectrometer; or, selectively, the concentration of at least one of these ions.

METHOD FOR CARRYING OUT ION MOBILITY SPECTROMETRY ANALYSES

The present invention relates to differential methods for carrying out ion mobility spectrometry analyses, and in particular the simultaneous analysis of more impurities contained in a very pure gas, such as those employed in the microelectronic industry.

Ion mobility spectrometry is generally known in the field of chemical analyses with the abbreviation IMS, which also indicates the instrument for carrying out the analytic technique (in this case abbreviating the terms Ion Mobility Spectrometer).

The interest for the IMS technique comes from its extremely high sensitivity, associated with the reduced size and cost of the instrument. By operating in suitable conditions it is possible to detect species in gas or vapor phase in a gas mixture in picograms quantities (pg, i.e. 10^{-12} grams), or in part per trillion concentrations (ppt, equal to a molecule of analyzed substance per 10^{12} molecules of sample gas); the gas forming most of the gas mixture will be called "carrier gas" from now on, while the mixture itself will be called "sample gas".

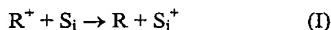
There are many application fields of this technique, both in civilian sectors (in particular, for the detection in the industry of inorganic or organic contaminants in clean rooms or of noxious species in the industrial exhausts) and in military sectors (in particular, for the detection of the presence of explosive or toxic substances, such as nerve gases). IMS analysis methods and instruments are disclosed, for example, in US patents 5,457,316, 5,955,886 and 6,229,143.

The general geometrical structure of an IMS instrument is shown in the only attached drawing. The instrument is essentially made up of a cylindrical chamber C having at one end the inlet IC for the sample gas, around which an inlet electrode ER and a ionizing member IM are arranged, and at the opposite end a detector D for charged particles. Detector D is normally kept at the ground potential, while the inlet electrode ER is kept at a potential higher than that of the detector (instrument working in the positive mode) or lower (negative mode) than said detector potential; in the remainder of the description reference will always be made to the use of an IMS instrument in the positive mode (the ions corresponding to the analyzed species will be

- 2 -

indicated as positive ions), which corresponds to the most common condition of use, but all these considerations are also valid for the use in the negative mode. An electrifiable grid G divides chamber C into two zones, referred to in the field as the "reaction zone" (on the inlet side of the instrument; indicated in the following with RZ) and the "drift zone" (on the detector side of the instrument; indicated in the following with DZ). Grid G generally comprises two alternated series of linear and parallel conductive members, commonly metal wires, which are arranged perpendicularly to the longitudinal axis x of chamber C. A series of electrodes E_i ($i=1, \dots, n$), generally annular, each set at a suitable voltage for creating between the inlet electrode ER and detector D an electric field suitable for transporting the ions toward said detector, is arranged along the walls of the two zones RZ and DZ. A screen grid SG is arranged between the last electrode E_n and detector D to avoid the creation on the latter of an "image charge", that is, the build up of an electrostatically induced charge on detector D. The wires of grid G are inserted into the central cavity of an electrode E_g , defined from now on as grid electrode, from which are however electrically insulated. During their motion, the ions are slowed down by a gas usually counter-flowing with respect to the ion motion direction. This gas is introduced from a duct DC at the end of chamber C where detector D is located and is expelled by an outlet OC at the opposite end; the counter-flowing gas, defined as "drift gas" in the field, is a ultra-pure gas which can be the same as the carrier gas or different.

The ionizing member is IM commonly a beta radiation source comprising ^{63}Ni . According to the working mode, the ions with a charge opposite to the charge of the inlet electrode ER are neutralized on the same, while the ions with a charge of the same sign as this electrode undergo a repulsion and are accelerated in the reaction zone. The first ionization produces essentially exclusively ions of the carrier gas, due to its concentration higher by several orders of magnitude than that of the other species, generally present as traces; the primary ions corresponding to the carrier gas are called "reactant ions" in the field. In the reaction zone the charge of the reactant ions is distributed among the present species according to their electron or proton affinities, to their ionization potentials or to their electronegativity, according to reactions of the kind:



- 3 -

wherein R^+ represents a reactant ion, R a neutral molecule deriving from the neutralization of the reactant ion (that is, a carrier gas molecule), S_i ($i=1, \dots, n$) a molecule of the i -th species to be analyzed and S_i^+ the ion corresponding to S_i ; the ions S_i^+ often give rise to complex species due to the association with one or more neutral molecules, but for notation easiness and without losing generality, reference will always be made to simple ions from now on.

All these ions are transported by the electric field toward the electrifiable grid G. The grid members are grouped in two mutually alternated series, so that each member of one series has two members of the other series as the closest members; the two series of grid members are normally biased with potential values higher and lower, respectively, than the potential of the grid electrode E_g . A transversal electric field generally stronger than the one along the longitudinal axis of the chamber in that point is thus created on the grid plane, so that the ions present in the reaction zone are accelerated toward the members of one of the two series constituting the grid and neutralized: in these conditions, the grid is "closed" and prevents the ions from passing toward the drift zone. When the analysis is to be carried out, the two series of grid members are brought at the same potential of the grid electrode, thereby canceling the transversal field: in these conditions the grid is "open" so that the ions can advance into the drift zone. The grid opening lasts generally from some tens to some hundreds of microseconds and during this time a portion of the ions present in the reaction zone is transferred to the drift zone. In particular, the grid is crossed by the ions contained in a cylindrical volume in the reaction zone adjacent to the grid, the height of which is determined by the relation:

$$l_a = v_i \times t_a \quad (II)$$

where l_a is the height of the cylindrical volume, v_i is the motion speed of the ion S_i^+ and t_a is the opening time of the grid. The initial or central instant of the grid opening time slot is commonly assumed as the "time zero", that is, the analysis start.

In the drift zone DZ the ions are transported toward detector D with a motion speed which is the resultant of the acceleration due to the presence of the axial electric field and the deceleration due to the collisions with the drift gas. In particular, the motion speed of the i -th ion depends linearly on the electric field and is directly

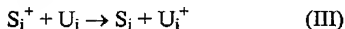
- 4 -

proportional to the temperature T and inversely proportional to the pressure P , according to the effect that the latter two terms have on the viscosity of the drift gas. While the acceleration due to the electric field acts to the same extent on the ions having the same charge (but in the IMS all the ions generally have a unitary charge), the deceleration acts in a different way on the ions according to the different size, shape and mass of the same, so that each ion has a characteristic motion speed and therefore a crossing time of the drift zone (defined as "drift time" in the field) generally different from that of the other ions. By recording the charges collected on detector D a spectrum is obtained comprising ion current peaks as a function of the time elapsed from the test start. The intensity of each peak in the spectrum is proportional to the amount of charge, $C_{S_i^+}$, transported by the ion S_i^+ which caused the peak.

Through calibrating tests, in which sample gases containing a single species S_i are analyzed, it is possible, in principle, to obtain data such as speed and drift time of the ionic species S_i^+ in a given gas and at given temperature and pressure conditions, as well as the efficiency of the reaction I for that species. In ideal conditions and operating in the same conditions of the calibrating tests, these data could be employed in an IMS analysis for determining the presence of a species S_i in the gas under exam according to the position of the peaks in the spectrum, and its concentration according to the relative size of the different peaks.

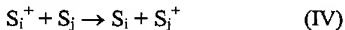
However, in the real analyses the situation is much more complex, due to many phenomena which affect the above theoretical conditions.

A first phenomenon consists in the possible presence of unexpected and unknown species U_i ($i=1, \dots, m$), for which calibration data are not available and that may interfere with the analysis by subtracting charge from the ions S_i^+ or from the ions R^+ according to reactions of the kind:

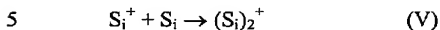


The result is a spectrum in which the peaks relating to the ions S_i^+ and the peak relating to the ion R^+ (defined in the field "reactant ion peak", or with its abbreviation RIP, which will be adopted in the following) have an intensity lower than in theoretical conditions or may even disappear, while there are peaks which cannot have an attribution.

Furthermore, the species formed in the reaction zone may react with other neutral species, already in the reaction zone or in the drift zone, with reactions of the kind:



or



each of which proceeds to different degrees and at different rates according to the different kinetics and equilibrium constants for each reaction. These reactions cause the modification of the concentrations of the ions reaching the detector of the IMS instrument with respect to the concentrations initially formed by the direct reaction with the R^+ ions, so that the ions corresponding to a species could completely disappear and the latter cannot be detected anymore in the analysis. Reference can be made to the book "Ion Mobility Spectrometry", edited by G. A. Eiceman and Z. Karpas, published in 1994 by CRC Press, for a presentation of the complex charge transfer principles involved in these reactions.

Furthermore, gases like O_2 , CO , H_2 , H_2O , etc., coming for instance from previous analyses, can be present on the inner surfaces of the instrument (such as the inner walls of the chamber, electrodes, etc.), either chemisorbed or physically adsorbed. Alternatively, these gases can be dissolved in the materials constituting the instrument; for example steel, which the chamber is generally made of, normally contains hydrogen.

These gases are released both in the reaction zone and in the drift zone. During the analysis, they form additional species B_i ($i=1, \dots, r$) which come into reactions of type I, III or IV. When these reactions occur in the reaction zone, a charge is removed from the species initially present in the sample gas and spurious peaks appear in the final spectrum. The same reactions, when they occur in the drift zone, may instead lead to spectrum distortions: in fact, unlike the ions of the species S_i , which come into the drift zone all at the same time and start from the same position (the grid), the ions corresponding to these species are formed at different points of the drift zone, and therefore reach the detector at different times according to the formation point: the consequence is that between the spectrum peaks the baseline is not zero as it should be in theory, but there is instead a non-null spectrum "background", which complicates the determination of the area of the peaks or may make it practically impossible in the case

- 6 -

of peaks with a lower intensity. The presence of the species B_i also involves other drawbacks: first, these may react with species S_i^+ through reactions of type III or IV in the drift zone, thus causing an undesired attenuation of the charge quantity transferred by the species S_i^+ to the detector and a consequent reduction of the instrument sensitivity; second, the interaction of species B_i with the species R^+ in the drift zone may cause an undesired attenuation of the RIP, with a consequent reduction of the upper reading threshold of the instrument.

It is therefore an object of the present invention to overcome or at least minimize the above mentioned problems of the IMS analyses.

Said object is achieved with a method, the main features of which are disclosed in claim 1, while other features are disclosed in the remaining claims.

Further advantages and features of the method according to the present invention will become clear to those skilled in the art from the following detailed and non-limiting description of some embodiments thereof, with reference to the sole figure, which shows a longitudinal cross-section view of the chamber of an IMS instrument:

It is generally acknowledged that an IMS spectrum could in principle be interpreted and fully analyzed, thereby obtaining the concentration of the species present as impurities in the gas under analysis. However, such interpretation is complicated by the need to know several numeric parameters that are very difficult to determine; in particular, to carry out a complete interpretation of an IMS spectrum, one should know all of the kinetic constants K_{R-S_i} for reactions of type I, as well as the kinetic constants $K_{S_i-S_j}$ and $K_{S_i-U_j}$ of side reactions of type III and IV. The values of these constants for each species S_i could be obtained through a suitable calibration procedure, but that would require an extremely long and burdensome set of preparatory tests. The problem is generally faced by making assumptions on the phenomena occurring during the analysis, e.g., that the entity of side-reactions of type III, IV and V, or with species B_i , can be neglected; this leads to a simplification of the calculations, but is an approximation that introduces errors in the result of the analysis.

The method of the invention consists in carrying out two subsequent analyses with the IMS instrument changing one parameter in the two tests, obtaining a series of data (defined as "primary data" from now on) from the two spectra obtained as direct results

of the analysis, and employing the primary data of the two analyses in a mathematical relation thus obtaining two equations, each one relating to one of the two subsequent analyses; by comparing these two equations (in particular, dividing one by another) it is possible to eliminate from the calculation the unknown values or parameters that are generally neglected in the prior art method; this allows to perform calculations that lead to the final results of the analysis, expressed as the concentration of at least one of the species S_i ($i=1, \dots, n$), that are not affected by the approximation problems of the prior art. Of course, in the methods of the invention, all experimental parameters apart from the one intentionally changed remain unchanged in the two subsequent analyses.

In a first embodiment thereof, the method of the invention consists in carrying out two IMS tests in such experimental conditions as to modify the residence time of the ionic species S_i^+ in the reaction zone of the IMS spectrometer.

During their experimental activity, the inventors have determined that the amount of charge, C_{Si}^+ , transported by the ion S_i^+ onto detector D can be represented by the following equation:

$$C_{Si}^+ = [S_i] \times t \times \Delta \times K_{R-Si} / \xi \times \gamma^t \quad (VI)$$

wherein:

- $[S_i]$ is the concentration of the species S_i ;
- t is the residence time of the ion S_i^+ in the reaction zone RZ, which can be calculated from known quantities, such as the flow speed of the sample gas and of the drift gas, the intensity of the electric field in the reaction zone, the intensity of the electric field in the drift zone, the length of the reaction zone, the length of the drift zone; alternatively, t can be derived from measurable quantities, such as the time of flight of the ion S_i^+ ;
- Δ is the difference between the charge quantity directly formed by the ionizing member IM, $C_{R,0}$, and the charge transported onto detector D by the ion R^+ , C_R ; Δ is equal to the charge transferred by the reactant ion and therefore to the total charge of all the species S_i^+ ($i=1, \dots, n$), U_i^+ ($i=1, \dots, m$), and can thus be obtained by the spectrum resulting from the IMS analysis by calculating the area bounded below all the peaks present in the spectrum (comprising the area bounded below the baseline), except the RIP;

- 8 -

- K_{R-S_i} is the kinetic constant of the charge transfer reaction from the ion R^+ to the species S_i (reaction of type I);
- ξ is equal to $\ln (C_{R,0}/C_R)$ and can be obtained from the spectrum resulting from the IMS analysis by knowing the area bounded below all the peaks present in the spectrum (comprising the area bounded below the baseline) and the area of the RIP only;
- γ is a function which considers the reaction constants $K_{S_i-S_j}$ and $K_{S_i-U_j}$ between the species S_i and all the species S_j^+ ($j=1, \dots, n; j \neq i$), U_j^+ ($j=1, \dots, m$) and between the species S_i^+ and all the species S_j ($j=1, \dots, n$), U_j ($j=1, \dots, m$) (reactions of type III, IV or V); γ also considers the concentrations of all the species S_j ($j=1, \dots, n; j \neq i$), U_j ($j=1, \dots, m$), i.e. of all the species except S_i , but including for instance the species U_i and B_i ; as IMS analyses are very quick, and carrying out a complete set of tests required for performing a differential method of the invention takes times in the order of seconds, the approximation can be made that these concentrations remain constant during an analysis according to the invention; in these conditions, this function assumes a fixed value. The exponent t in the term γ^t which appears in the equation has the same meaning explained above.

In equation VI, $[S_i]$ is the datum which is to be determined at the end of the analysis and therefore is not a parameter which the operator can modify at will; the terms Δ , K_{R-S_i} , ξ and γ^t express intrinsic chemical reactivity features of the species present in the analyzed system, and thus are out of operator's control as well. Vice versa, the operator of the analysis can modify at pleasure (within certain limits) the terms $C_{S_i}^+$ and t , and therefore these represent "control parameters" of the method of the invention.

The residence time of the species S_i^+ in the reaction zone, t , can be modified through several practical methods. A first way is to change in the two tests the value of the electrical field in said zone; in turn this can be achieved by varying in the two tests the electrical field in the whole instrument, or selectively only in zone RZ. This second possibility can be realized by using the IMS instrument that is the object of co-pending Italian patent application No. MI2002A001616. As described in said Italian application, the instrument allows to control the electrical field applied in the chamber of the

instrument, and in particular to obtain fields with a non-uniform profile along the x axis of said chamber. The preferred kind of non-uniform electrical field is that made up of the sum of two different electrical fields in the zones RZ and DZ; these two electrical field will be referred to as E_{RZ} and E_{DZ} , respectively, and are preferably both uniform.

Considering the expression VI above, when the electric field E_{RZ} varies, the value of terms t , Δ and ξ changes, while the terms $[S_i]$ ($i=1, \dots, n$), $[U_j]$ ($j=1, \dots, m$), γ and the kinetic constants K_{R-Si} , K_{Si-Sj} and K_{Si-Uj} do not change. Therefore, by carrying out two tests with two different values of electric field E_{RZ} , two values, C_{1Si}^+ e C_{2Si}^+ , are obtained for the charge transported onto the detector by the species S_i^+ . By using the expression VI, the two charge values can be expressed as:

$$C_{1Si}^+ = [S_i] \times t_1 \times \Delta_1 \times K_{R-Si} / \xi_1 \times \gamma^{t_1} \quad (VII)$$

and

$$C_{2Si}^+ = [S_i] \times t_2 \times \Delta_2 \times K_{R-Si} / \xi_2 \times \gamma^{t_2} \quad (VIII)$$

wherein the subscripts 1 e 2 added with respect to the equation VI represent the two analyses carried out with a different field value. By dividing the expression VII by VIII the invariant terms are canceled, thereby obtaining:

$$C_{1Si}^+/C_{2Si}^+ = (t_1 \times \Delta_1 \times \xi_2) / (t_2 \times \Delta_2 \times \xi_1) \times \gamma^{(t_1-t_2)} \quad (IX)$$

The values of t_1 , t_2 , Δ_1 , Δ_2 , ξ_1 e ξ_2 and of the ratio C_{1Si}^+/C_{2Si}^+ can be obtained from the two spectra; with these, from equation IX is obtained the value of γ , which can be employed in equation VI for deducing $[S_i]$ without needing to know the reaction constants K_{Si-Sj} and K_{Si-Uj} .

The very same effect (i.e., the modification of the residence time of ions S_i^+ in the RZ) can be obtained also by modifying the ratio between the flow speeds of the sample gas, F_C , and of the drift gas, F_D , or by modifying the length of the reaction zone. The modification of the ratio F_C/F_D can be easily obtained by controlling the flow in the gas lines feeding the sample gas and the drift gas; this can simply be done with needle valves, mass-flow meters, or similar devices known to those skilled in the art; in using this method only one or both flow speeds can be changed in the two tests. The modification of the length of RZ can be obtained, for instance, by arranging two (or more) grids in the chamber of the spectrometer, at different points along the instrument axis, and by selectively activating only one of the two grids, that is, by alternatively

“opening” only one of the two grids in the different tests; an IMS instrument provided with two grids is known for example by US Pat. No. 5,200,614, but in this patent the presence of the two grids is used in a different way for a different reason, i.e., for creating a zone in the instrument with an essentially null electric field. As the effect is the same as that obtained by varying E_{RZ} , the analysis method is the same too, namely, expressions VII through IX are employed to obtain the value of γ that’s then employed in expression VI to evaluate the concentration of the species S_i .

A second embodiment of the differential method of the invention consists in carrying out two different tests at different values of electric field applied in the drift zone, E_{DZ} , and comparing the results thus obtained. The variation in the time of the electric field E_{DZ} allows to solve the non-ideality due to the secondary reactions which take place in the drift zone among the ions S_i^+ and the species B_i released by the inner parts of the instrument. The inventors have found that the charge transferred to detector D by the ions S_i^+ (indicated in the following as C_{A,Si^+}) is linked to the charge quantity actually connected to the ion S_i^+ (indicated with C_{Si^+}) which comes into the drift zone DZ at the opening of grid G through the relation:

$$C_{A,Si^+} = C_{Si^+} \times \lambda^i \quad (X)$$

where λ is a function which considers the charge transfer constants, K_{Si-Bj} , between the ions S_i^+ and the different additional species B_i ($i=1, \dots, r$), released by the material constituting the inner parts of the instrument, and the concentrations $[B_i]$ ($i=1, \dots, r$) of these species. By carrying out two tests at different time slots, with a different electric field E_{DZ} in the two tests, the following two relations can be written:

$$C_{1A,Si^+} = C_{Si^+} \times \lambda^{t1} \quad (XI)$$

and

$$C_{2A,Si^+} = C_{Si^+} \times \lambda^{t2} \quad (XII)$$

The meaning of the symbols in these relations is analogous to that of the symbols in the equations VII and VIII

By dividing the equation XI by XII the following equation results:

$$C_{1A,Si^+}/C_{2A,Si^+} = \lambda^{(t1-t2)} \quad (XIII)$$

from which λ is obtained by measuring the times t_1 and t_2 in the spectra and obtaining C_{1A,Si^+} and C_{2A,Si^+} from the areas of the peaks relevant to the species S_i^+ ; once

λ is known, and by measuring $C_{A,Si}^+$, it is possible to deduce the exact value of C_{Si}^+ from the relation X, and therefore the value of the concentration of the species S_i in the sample gas from the relation VI.

In its third embodiment, the method of the invention consists in carrying out two IMS tests in such experimental conditions as to modify the value of C_{Si}^+ . In this case, a pair of tests for each species S_i is needed for carrying out a complete analysis of the sample gas: however, the first test can be common to all the pairs of tests. The value of C_{Si}^+ can be modified by adding a known concentration of the species S_i to the sample gas. In these conditions, the charge quantity transported to detector D by the i-th species can be described for the two tests by these equations, respectively:

$$C_{1Si}^+ = [S_i] \times t \times \Delta_1 \times K_{R-Si} / \xi_1 \times \gamma^i \quad (XIV)$$

and

$$C_{2Si}^+ = ([S_i] + x) \times t \times \Delta_2 \times K_{R-Si} / \xi_2 \times \gamma^i \quad (XV)$$

wherein x represents the known concentration of species S_i added in the second

test.

In this case, the residence time of the i-th species in the reaction zone remains unchanged, so that in the equations XIV and XV there are no subscripts 1 and 2 for this parameter. The following equation is obtained by dividing equation XIV by XV:

$$C_{1Si}^+ / C_{2Si}^+ = [S_i] / ([S_i] + x) \times (\Delta_1 \times \xi_2) / (\Delta_2 \times \xi_1) \quad (XVI)$$

Also in this case, the values of C_{1Si}^+ , C_{2Si}^+ , Δ_1 , Δ_2 , ξ_1 and ξ_2 are obtained from the spectra relating to the two tests; since the term x is known, the only remaining unknown quantity remains $[S_i]$, which can be therefore easily obtained from the previous expression.

The methods of the invention thus allow to overcome the problems of interpretation of IMS spectra of the prior art, avoiding the need to know all the reactions which take place in the instrument chamber and all the relevant kinetic constants, and the need to solve a matrix comprising a number of equations equal to the number of primary reactions of type I and secondary reactions of type III, IV or V. Gathering these data, which could be done through complex calibrating procedures, would lead to an extremely burdensome method. Furthermore, also performing a calibration, it would be impossible to consider the reactions of type III, i.e. reactions which take place in the real

- 12 -

analysis conditions with unexpected or unknown species. In particular, the first and third described embodiments allow to solve the non-ideality problems of the technique due to the presence of secondary reactions of type III, IV and V, while the second described embodiment allows to solve the non-ideality problems due to the presence of species of type B_i in the instrument chamber.

In any embodiments of the method, the spectrum representing the result of the analysis is preferably processed in an automatic way by a suitable known programmable control unit with a microprocessor, for example a computer provided with suitable interfaces; the values C_{1Si}^{+} , C_{2Si}^{+} , $C_{1A,Si}^{+}$, $C_{2A,Si}^{+}$, t_1 , t_2 , Δ_1 , Δ_2 , ξ_1 and ξ_2 , which an operator can employ for obtaining the concentrations of the species S_i (i=1, ..., n) as above described, are obtained as primary data as a result of this automatic analysis. As a preferred alternative, the same unit that analyzes the spectrum, thereby generating the primary data, uses these same data for processing the equations VI to XVI and directly supplies the values of the concentrations of the species S_i.

15

CLAIMS

1. Method for carrying out analyses of a gas comprising one or more species S_i ($i=1, \dots, n$) by means of ion mobility spectrometry, comprising the steps of:

- 5 – carrying out a first test with a first set of values of the experimental parameters;
- carrying out a second test with a second set of values of the experimental parameters, such as that one parameter chosen among the concentration $[S_i]$ of the species giving rise to ions S_i^+ ($i=1, \dots, n$), the residence time of said ions in the reaction zone or the residence time of said ions in the drift zone of an ion mobility spectrometer differs
- 10 from the value of the corresponding parameter of said first set;
- employing the data obtained in said two tests in a relation expressing the charge transferred by the i -th ion to the detector of said spectrometer, C_{Si}^+ , as a function of test parameters, thereby obtaining two equations;
- dividing said two equations by one another, thus eliminating from the calculation
- 15 invariant parameters, and obtaining as a result of said division at least one parameter that can then be reintroduced in each of the two equations above, thereby obtaining the concentration $[S_i]$ of at least one of the species S_i ($i=1, \dots, n$).

2. Method according to claim 1, wherein said relation is:

$$C_{Si}^+ = [S_i] \times t \times \Delta \times K_{R-Si} / \xi \times \gamma^t$$

- 20 wherein the parameter changed in said two tests is the residence time t of the ions S_i^+ ($i=1, \dots, n$) in the reaction zone of the ion mobility spectrometer, said method comprising the following steps:

- carrying out said first test, thereby deducing from the obtained spectrum the values of the terms C_{1Si}^+ , t_1 , Δ_1 , and ξ_1 in the conditions of said first test;
- 25 – carrying out said second test, thereby deducing from the obtained spectrum the values of the terms C_{2Si}^+ , t_2 , Δ_2 , and ξ_2 in the conditions of said second test;
- employing said values for obtaining the following two equations:

$$C_{1Si}^+ = [S_i] \times t_1 \times \Delta_1 \times K_{R-Si} / \xi_1 \times \gamma^{t_1}$$

and

30 $C_{2Si}^+ = [S_i] \times t_2 \times \Delta_2 \times K_{R-Si} / \xi_2 \times \gamma^{t_2};$

- dividing the first of said equations by the second one, thereby obtaining this

- 14 -

equation:

$$C_{1Si}^+/C_{2Si}^+ = (t_1 \times \Delta_1 \times \xi_2) / (t_2 \times \Delta_2 \times \xi_1) \times \gamma^{(1-2)};$$

- obtaining the value of γ from the latter equation; and
- employing the so obtained value of γ in the expression:

5
$$C_{1Si}^+ = [S_i] \times t_1 \times \Delta_1 \times K_{R-Si} / \xi_1 \times \gamma^{t_1}$$

for obtaining the value of $[S_i]$ for at least one of the species S_i ($i=1, \dots, n$).

3. Method according to claim 2, wherein t is changed by varying the electrical field in the reaction zone of the instrument, E_{RZ} .

4. Method according to claim 2, wherein t is changed by varying the ratio
10 between the flow speed of the sample gas, F_C , and the flow speed of the counter-flowing gas, F_D .

5. Method according to claim 2, wherein t is changed by varying the length of the reaction zone by providing an IMS instrument with two grids arranged at different positions along the axis of the ion mobility spectrometer and activating
15 selectively one of the two grids in each of said two tests.

6. Method according to claim 1, wherein said relation is:

$$C_{Si}^+ = [S_i] \times t \times \Delta \times K_{R-Si} / \xi \times \gamma^t$$

wherein the parameter changed in said two tests is the concentration $[S_i]$ of at least one of the ions S_i^+ ($i=1, \dots, n$), said change being obtained by adding a known concentration,
20 x , of the species S_i to the sample gas, said method comprising the following steps:

- carrying out said first test, thereby deducing from the obtained spectrum the values of the terms C_{1Si}^+ , Δ_1 , and ξ_1 in the conditions of said first test;
- carrying out said second test, thereby deducing from the obtained spectrum the values of the terms C_{2Si}^+ , Δ_2 , and ξ_2 in the conditions of said second test;
- 25 - employing said values for obtaining the following two equations:

$$C_{1Si}^+ = [S_i] \times t \times \Delta_1 \times K_{R-Si} / \xi_1 \times \gamma^{t_1}$$

and

$$C_{2Si}^+ = ([S_i] + x) \times t \times \Delta_2 \times K_{R-Si} / \xi_2 \times \gamma^{t_2};$$

- dividing the first of said equations by the second one, thereby obtaining this
30 equation:

$$C_{1Si}^+/C_{2Si}^+ = [S_i] / ([S_i] + x) \times (\Delta_1 \times \xi_2) / (\Delta_2 \times \xi_1); \text{ and}$$

- 15 -

- obtaining from the latter equation the value of $[S_i]$ for at least one of the species S_i ($i=1, \dots, n$).

7. Method according to claim 1, wherein said relation is:

$$C_{A,Si}^+ = C_{Si}^+ \times \lambda^1$$

- 5 wherein the parameter changed in said two tests is the residence time of ions in the drift zone of the ion mobility spectrometer, said change being obtained by varying the electrical field in the drift zone of the instrument, E_{DZ} , said method comprising the following steps:

- carrying out said first test, deducing from the obtained spectrum the value of the terms $C_{1A,Si}^+$ and t_1 in the conditions of said first test;
- 10 - carrying out said second test, deducing from the obtained spectrum the value of the terms $C_{2A,Si}^+$ and t_2 in the conditions of said second test;
- employing said values for obtaining the following two equations:

$$C_{1A,Si}^+ = C_{Si}^+ \times \lambda^{t_1}$$

- 15 and

$$C_{2A,Si}^+ = C_{Si}^+ \times \lambda^{t_2}$$

- dividing the first of said equations by the second one, thereby obtaining this equation:

$$C_{1A,Si}^+ / C_{2A,Si}^+ = \lambda^{(t_1 - t_2)}$$

- 20 - obtaining the value of λ from the latter equation;
- employing the so obtained value of λ in the expression:

$$C_{1A,Si}^+ = C_{Si}^+ \times \lambda^{t_1}$$

for obtaining the value of C_{Si}^+ ; and

- introducing the so obtained value of C_{Si}^+ in the equation:

25
$$C_{Si}^+ = [S_i] \times t \times \Delta \times K_{R-Si} / \xi \times \gamma^t$$

for obtaining the value of $[S_i]$ for at least one of the species S_i ($i=1, \dots, n$).

8. Method according to any of claims 2, 6 or 7, wherein the values of the terms C_{1Si}^+ , C_{2Si}^+ , $C_{1A,Si}^+$, $C_{2A,Si}^+$, t_1 , t_2 , Δ_1 , Δ_2 , ξ_1 and ξ_2 are obtained from the spectra resulting from said tests in an automatic way by a programmable control unit with a

30 microprocessor.

9. Method according to claim 8, wherein said unit uses said values for

- 16 -

directly supplying the values of the concentrations of the species S_i .

10. Method according to one of claims 8 or 9, wherein said unit is a computer provided with interfaces for the connection with the ion mobility spectrometer.

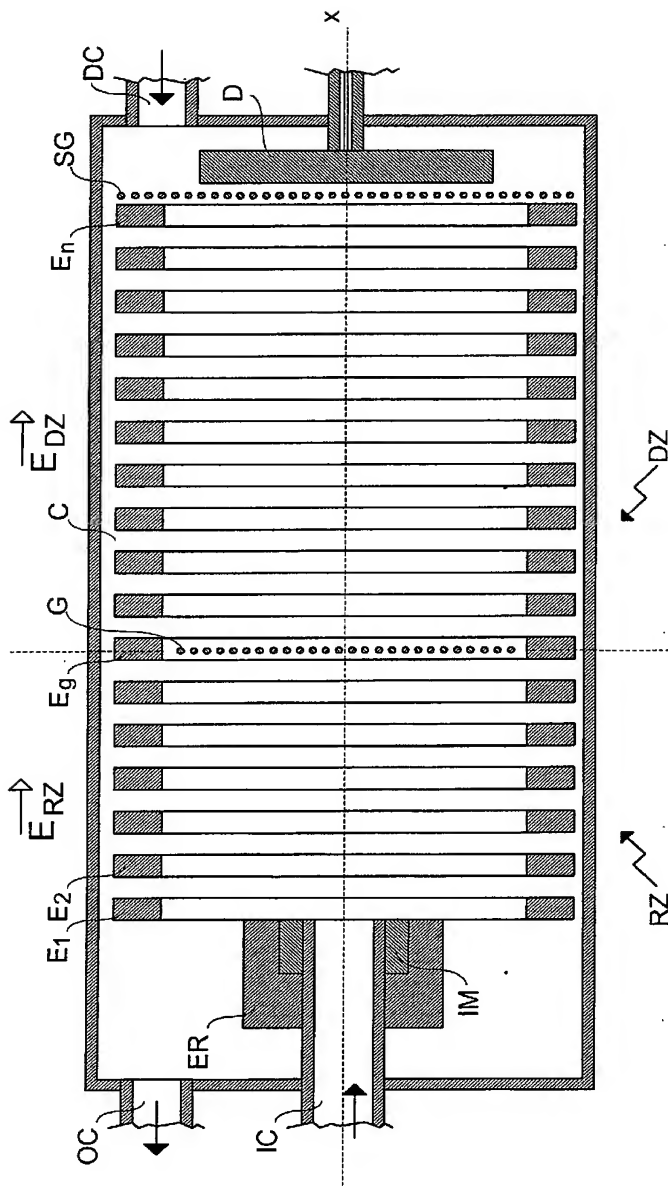


Fig. 1

INTERNATIONAL SEARCH REPORT

PCT/IT 03/00429

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G01N27/64 G01N33/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 6 291 821 B1 (KUJA FRANK ET AL) 18 September 2001 (2001-09-18) the whole document ---	1 2-10
X A	US 5 723 861 A (TARASSOV ALEXANDER SEMENTOVICH ET AL) 3 March 1998 (1998-03-03) abstract column 2, line 48 -column 7, line 33 ---	1 6
X	US 6 011 258 A (ALBERTI SEGUNDO SANDRA MARA ET AL) 4 January 2000 (2000-01-04) claims 1,2 --- -/-	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

S document member of the same patent family

Date of the actual completion of the international search

1 October 2003

Date of mailing of the international search report

14/10/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5618 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl
Fax: (+31-70) 340-3016

Authorized officer

Klein, M-O

INTERNATIONAL SEARCH REPORT

PCT/IT 03/00429

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02 052255 A (GETTERS SPA ;PUSTERLA LUCA (IT); SUCCI MARCO (IT); BONUCCI ANTONIO) 4 July 2002 (2002-07-04) the whole document ----	1-10
A	US 5 405 781 A (DAVIES JOHN H ET AL) 11 April 1995 (1995-04-11) the whole document ----	1-10
A	US 5 510 268 A (DOERING HANS-RUEDIGER ET AL) 23 April 1996 (1996-04-23) the whole document ----	1-10
P,X	WO 02 099405 A (GETTERS SPA ;PUSTERLA LUCA (IT); SUCCI MARCO (IT); BONUCCI ANTONIO) 12 December 2002 (2002-12-12) the whole document -----	1

INTERNATIONAL SEARCH REPORT

PCT/IT 03/00429

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 6291821	B1	18-09-2001	CA	2291546 A1	02-06-2001
US 5723861	A	03-03-1998	AU	2440797 A	29-10-1997
			CA	2250145 A1	16-10-1997
			EP	0891543 A1	20-01-1999
			FI	982140 A	02-10-1998
			IL	126355 A	13-09-2001
			JP	2000509487 T	25-07-2000
			WO	9738302 A1	16-10-1997
			US	5736739 A	07-04-1998
US 6011258	A	04-01-2000	DE	19528290 C1	23-01-1997
			BR	9609808 A	06-07-1999
			WO	9705635 A1	13-02-1997
			EP	0842522 A1	20-05-1998
WO 02052255	A	04-07-2002	IT	MI20002830 A1	24-06-2002
			CA	2427015 A1	04-07-2002
			CZ	20031425 A3	13-08-2003
			WO	02052255 A1	04-07-2002
US 5405781	A	11-04-1995	CA	2132607 A1	22-03-1995
US 5510268	A	23-04-1996	NONE		
WO 02099405	A	12-12-2002	IT	MI20011193 A1	06-12-2002
			WO	02099405 A2	12-12-2002